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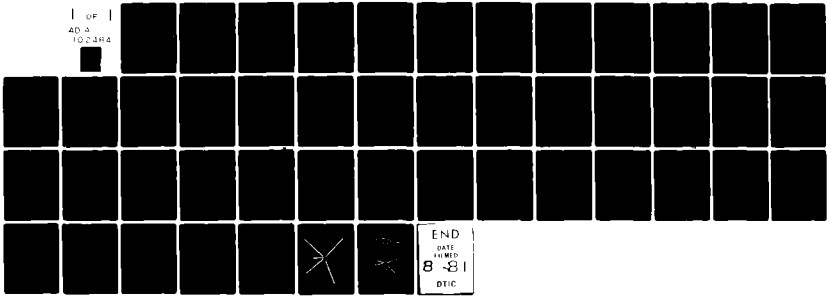

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Four tin(II) dithiophosphate esters, $Sn[S_2P(OR)_2]_2$, where R = $CH_3$, $C_2H_5$, $\underline{i}$-$C_3H_7$ and $C_6H_5$ are synthesized in high yield by the action of the $\underline{O},\underline{O}'$-diorgano-dithiophosphoric acids on dimethoxytin(II) in benzene to release methanol. The R = $C_2H_5$ product is a pale yellow oil, but the others are colorless crystalline solids soluble in non-polar organic solvents. The 2,2'-bipyridyl adducts of the parent esters form immediately upon mixing. NMR coupling is observed from the ester groups to phorphorus, as $|^3J(^{31}P\text{-}O\text{-}C\text{-}^1H)|$ = 15.5 Hz in the R = $CH_3$ derivative. Infrared spectral assignments can be made for the

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4. phosphato]tin(II), a Bicyclic Dimer of Circumscribed SnSSnS and SnSPSSnSPS Rings Held Together by Bifurcated S-$Sn_2$ Linkages Involving Three-Coordinated Sulfur Atoms and by $\underline{h}^6$-$C_6H_5$ Interactions Binding Tin(II) Lone Pairs to Phenoxy Ester Groups of Adjacent Molecules.

20. $\nu_{asym}$ ($PS_2$) (660-627 $cm^{-1}$), $\nu_{sym}$($PS_2$) (525-505 $cm^{-1}$), $\nu$[(P)O-C] (1190-1150 $cm^{-1}$), $\nu$[P-O(C)] (1030-1010 $cm^{-1}$) and $\nu$(SnS) (355-332 $cm^{-1}$) modes. In the mass spectra parent molecular ions are found for all the species, but the fragments resulting from the loss of one ligand moiety are more abundant. The chief pathway for the decomposition is the successive loss of ligand moieties. Ditin-bearing ions are detected in the spectrum of the R = $C_2H_5$ derivative. The mass spectra of the bipyridyl adducts are the superposition of those of the parent tin(II) esters and of bipyridyl. The tin-119m Mössbauer isomer shifts (IS = 3.66-3.78 mm $s^{-1}$) confirm the presence of tin (II) and the barely resolvable quadrupole splittings (QS = 0.97-1.06 mm $s^{-1}$) do not increase an complexation by bipyridyl (1.03-1.15 mm $s^{-1}$), suggesting that the parent tin(II) esters themselves have higher coordination number in the solid state. Bis-(O,O'-diphenyldithiophosphato)tin(II), $C_{24}H_{20}O_4S_4P_2Sn$, crystallizes in the triclinic space group $P\bar{1}$ with $\underline{a}$ = 10.4999(5)Å, $\underline{b}$ = 13.948(7) Å, c = 9.291(4) Å, $\alpha$ = 99.18(6)°, $\beta$ = 95.71(5)°, $\gamma$ = 91.80(5)°, at 138 ± 2K. The structure was determined by Patterson and Fourier techniques from 5517 reflections measured at 138 ± 2K on an automatic diffractometer using monochromated $MoK_\alpha$ radiation and refined to a final R value of 0.029 for all data, The centrosymmetric dimer contains one ligand bridging two tin atoms intermolecularly, while simultaneously chelating one tin atom in an extremely anisobidentate fashion via a bifurcated, three-coordinated sulfur atom [S(4)]. A second ligand is involved in normal chelation. Completing the coordination sphere at the tin(II) atom and contributing to the formation of the dimer is an $\underline{h}^6$-$C_6H_5$ interaction between the phenoxy ester group of the bridging ligand of the second molecular unit and the tin(II) lone pair to produce a $\psi$-6 coordinated metal center. A planar $Sn_2S_2$ ring is confirmed on inspection of the phosphorus distances to the sulfur atoms that make it up, and is seen to be circumscribed by an eight-membered $[SnSPS]_2$ ring in a chair conformation. The ester P(1)-S(1) and P(2)-S(3)-Sn(1) systems are distinguished from the double-bonded, dative P(1) = S(2) → Sn(1), P(2)=S(4)→Sn(1) and P(2')=S(4')→Sn(1) systems on the basis of their P-S and S-Sn internuclear distances. The tin atom is 0.50 Å out of the plane formed by the S(1), S(2), S(4) and S(4') atoms away from the S(3) atom, with the ester bound sulfur atoms cis-oriented [∢ S(1)-Sn(1)-Sn(3) = 87.41°]. The smallest angle in the plane is formed by the terminally chelating sulfur atoms [∢S(1)-Sn(1)-S(2) = 74.28°]. Atom S(3) is opposite the expected direction of the tin(II)-lone pair vector which if extended strikes a perpendicularly oriented phenoxy group with tin to carbon distances at 3.457 to 4.317 Å. The distances to the center of the ring and to the plane of the ring are 3.66 and 3.46 Å, respectively. The ordering of the angles at the phosphorus atoms obey the expected isovalent hybridization predictions: ∢ S-P-S > ∢ S-P-O > ∢ O-P-O. The stability of the phenoxy ester to air oxidation is rationalized in terms of the additional $\underline{h}^6$-$C_6H_5$ bonding contribution and by the steric blocking of the tin(II) lone pair by the phenoxy group.

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## ABSTRACT

Four tin(II) dithiophosphate esters, $Sn(S_2P(OR)_2)_2$, where R = $CH_3$, $C_2H_5$, $\underline{i}$-$C_3H_7$ and $C_6H_5$ are synthesized in high yield by the action of the $\underline{O},\underline{O}'$-diorganodithiophosphoric acids on dimethoxytin(II) in benzene to release methanol. The R = $C_2H_5$ product is a pale yellow oil, but the others are colorless crystalline solids soluble in non-polar organic solvents. The 2,2'-bipyridyl adducts of the parent esters form immediately upon mixing. NMR coupling is observed from the ester groups to phosphorus, as $|^3J(^{31}P\text{-}O\text{-}C\text{-}^1H)|$ = 15.5 Hz in the R = $CH_3$ derivative. Infrared spectral assignments can be made for the $\nu_{asym}$ ($PS_2$) (660-627 $cm^{-1}$), $\nu_{sym}$ ($PS_2$) (525-505 $cm^{-1}$), $\nu$[(P)O-C] (1190-1150 $cm^{-1}$), $\nu$[P-O(C)] (1030-1010 $cm^{-1}$) and $\nu$(SnS) (355-332 $cm^{-1}$) modes. In the mass spectra parent molecular ions are found for all the species, but the fragments resulting from the loss of one ligand moiety are more abundant. The chief pathway for the decomposition is the successive loss of ligand moieties. Ditin-bearing ions are detected in the spectrum of the R = $C_2H_5$ derivative. The mass spectra of the bipyridyl adducts are the superposition of those of the parent tin(II) esters and of bipyridyl. The tin-119m Mössbauer isomer shifts (IS = 3.66-3.78 mm $s^{-1}$) confirm the presence of tin(II) and the barely resolvable quadrupole splittings (QS = 0.97-1.06 mm $s^{-1}$) do not increase on complexation by bipyridyl (1.03-1.15 mm $s^{-1}$), suggesting that the parent tin(II) esters themselves have higher coordination number in the solid state. Bis-($\underline{O},\underline{O}'$-diphenyldithiophosphato)tin(II), $C_{24}H_{20}O_4S_4P_2Sn$, crystallizes in the triclinic space group $P\bar{1}$ with $\underline{a}$ = 10.499(5) Å, $\underline{b}$ = 13.948(7) Å, $\underline{c}$ = 9.291(4) Å, $\alpha$ = 99.18(6)°, $\beta$ = 95.71(5)°, $\gamma$ = 91.80(5)°, at 138 ± 2K. The structure was determined by Patterson and Fourier techniques from 5517 reflections measured at 138 ± 2K on an automatic diffractometer using monochromated $MoK_\alpha$ radiation and refined to a final R value of 0.029 for all

data. The centrosymmetric dimer contains one ligand bridging two tin atoms intermolecularly, while simultaneously chelating one tin atom in an extremely anisobidentate fashion via a bifurcated, three-coordinated sulfur atom [S(4)]. A second ligand is involved in normal chelation. Completing the coordination sphere at the tin(II) atom and contributing to the formation of the dimer is an $\underline{h}^6$-$C_6H_5$ interaction between the phenoxy ester group of the bridging ligand of the second molecular unit and the tin(II) lone pair to produce a $\psi$-6 coordinated metal center. A planar $Sn_2S_2$ ring is confirmed on inspection of the phosphorus distances to the sulfur atoms that make it up, and is seen to be circumscribed by an eight-membered $[SnSPS]_2$ ring in a chair conformation. The ester P(1)-S(1)-Sn(1) and P(2)-S(3)-Sn(1) systems are distinguished from the double-bonded, dative P(1) = S(2) → Sn(1), P(2)=S(4)→Sn(1) and P(2')=S(4')→Sn(1) systems on the basis of their P-S and S-Sn internuclear distances. The tin atom is 0.50 Å out of the plane formed by the S(1), S(2), S(4) and S(4') atoms away from the S(3) atom, with the ester bound sulfur atoms cis-oriented [$\measuredangle$ S(1)-Sn(1)-Sn(3) = 87.41°]. The smallest angle in the plane is formed by the terminally chelating sulfur atoms [$\measuredangle$ S(1)-Sn(1)-S(2) = 74.28°]. Atom S(3) is opposite the expected direction of the tin(II)-lone pair vector which if extended strikes a perpendicularly oriented phenoxy group with tin to carbon distances at 3.457 to 4.317 Å. The distances to the center of the ring and to the plane of the ring are 3.66 and 3.46 Å, respectively. The ordering of the angles at the phosphorus atoms obeys the expected isovalent hybridization predictions: $\measuredangle$ S-P-S > $\measuredangle$ S-P-O > $\measuredangle$ O-P-O. The stability of the phenoxy ester to air oxidation is rationalized in terms of the additional $\underline{h}^6$-$C_6H_5$ bonding contribution and by the steric blocking of the tin(II) lone pair by the phenoxy group.

In this series of papers we have been studying the synthetic routes to organotin(IV) derivatives of various oxy and thio phosphorus acids, and the spectroscopic properties and structures of the resulting products.[1] We have also had an interest in tin(II) chemistry extending over twenty years.[5] This paper is the issue of the marriage of these two themes. We report the synthesis of four tin(II) dithiophosphate esters, their adducts with 2,2'-bipyridyl and the remarkable and unexpected crystal structure of the diphenyl ester derivative.

## Experimental Section

The dithiophosphoric acids used in this study were prepared by literature methods.[6-9] Tin(II) dimethoxide was prepared from the reaction of tin(II) chloride and dry methanol in the presence of triethylamine.[10]

All solvents were dried and distilled immediately before use. Reactions were carried out under an atmosphere of dry nitrogen using standard aerobic techniques. With the exception of bis-(diphenyl dithiophosphato)tin(II) which is stable to atmospheric moisture for up to ca. 7 days, all the tin(II) dithiophosphate esters slowly turn orange on exposure to air. Infrared spectra were recorded as Nujol mulls or neat liquids on CsI plates or as KBr discs on a Beckman 4250 spectrometer. Tin-119 Mössbauer spectra were recorded at 77K on a Ranger Engineering constant acceleration spectrometer equipped with a proportional counter and with a $Ca^{119m}SnO_3$ source (New England Nuclear Corp.) and $Ca^{119}SnO_3$ used as the zero Isomer Shift (IS) reference standard at room temperature. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS system at 70 eV. NMR spectra were run on a Varian T60. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

### Bis-(O,O'-dimethoxydithiophosphato)tin(II), $Sn[S_2P(OCH_3)_2]_2$

To a suspension of dimethoxytin(II) (4.07g, 22.5mmol) in benzene (50mL) was added a solution of dimethoxydithiophosphoric acid (7.17g, 45.3mmol) in the same

solvent (20mL). During the course of a mildly exothermic reaction the insoluble starting material dissolved and small amounts of an insoluble brown product were formed. The mixture was stirred at room temperature for 48h, filtered under $N_2$, and the clear filtrate evaporated to dryness at reduced pressure, to leave a colorless solid product. Recrystallization from benzene/hexane (1:1) yielded the title compound (8.48g, 87%), m.p. 65.5-7°C.

Bis-(O,O'-diethyldithiophosphato)tin(II), $Sn[S_2P(OC_2H_5)_2]_2$

A suspension of dimethoxytin(II) (5.44g, 30.1mmol) in benzene (40mL) and a solution of diethyl dithiophosphoric acid (11.39g, 61.2mmol) in the same solvent (15mL) were stirred together at room temperature for 24h. The resulting mixture was filtered and the solvent removed from the filtrate to leave the product as a pale yellow oil (14.6g, 98.0%) which decomposed upon attempted distillation (ca. 80°C, 0.005torr).

Bis-(O,O'-diisopropyldithiophosphato)tin(II), $Sn[S_2P(OC_3H_7\text{-}i)_2]_2$

To a suspension of dimethoxytin(II) (3.62g, 20mmol) in benzene (20mL) was added a solution of diisopropyldithiophosphoric acid (4.28g, 40mmol) in benzene (20mL). After stirring at room temperature for 24h, the mixture was filtered (to remove traces of brown precipitate), concentrated in vacuo to yield an oil, which was then filtered again. On standing in vacuo at room temperature for ca. 3 weeks, the oil solidified to a colorless crystalline solid, which was washed with n-hexane (2x5mL) at -78°C and dried in vacuo (8.20g, 75.2%), m.p. 55-8°C.

Bis-(O,O'-diphenyldithiophosphato)tin(II), $Sn[S_2P(OC_6H_5)_2]_2$

Following the procedures outlined above, dimethoxytin(II) (5.89g, 32.6mmol) and diphenyldithiophosphoric acid (18.37g, 65.1mmol) were reacted in benzene (80mL). After 48h the mixture was filtered and concentrated to dryness. Recrystallization of the resulting solid from toluene/n-hexane (1:1) affords the

title compound as a colorless, crystalline solid (22.0g, 99.1%), m.p. 125.5-126.5°C.

The syntheses of all the 1:1 adducts of tin(II) dithiophosphates and 2,2'-bipyridyl follow essentially the same procedure; the synthesis of bis-(O,O'-diisopropyldithiophosphato)tin(II) 2,2'-bipyridyl (1:1) is given as a typical example.

Bis-(O,O'-diisopropyldithiophosphato)tin(II) 2,2'-bipyridyl (1:1), $Sn[S_2P(OC_3H_7\text{-}i)_2]_2 \cdot C_{10}H_8N_2$

Solutions of the tin(II) dithiophosphate (2.00g, 37mmol) and 2,2'-bipyridyl (0.60g, 3.8mmol) in n-hexane (10mL each) were mixed, with stirring, under a dry nitrogen atmosphere. A yellow precipitate formed immediately, and was isolated by filtration, washed with n-hexane and recrystallized from hexane/benzene (ca. 20:1) to yield the 1:1 adduct as a yellow crystalline solid (1.90g, 73.3%), m.p. 105-7°C.

Details of other adducts, $Sn[S_2P(OR)_2]_2 \cdot C_{10}H_8N_2$, prepared by this method are tabulated below.

Analytical and physical data for the esters and their bipyridyl adducts are tabulated in Table I, tin-119m Mössbauer data in Table II, proton NMR data in Table III, infrared data in Table IV and mass spectral data in Table V.

| R | gms (mmol) Dithiophosphate | gms (mmol) 2,2'-bipyridyl | Recrystallization Solvent | Yield(%) |
|---|---|---|---|---|
| $CH_3$ | 2.16 (5.0) in benzene (10mL) | 0.80 (5.1) in n-hexane (10mL) | n-hexane/benzene (2:1) | 1.50g (50.9) |
| $C_2H_5$ | 2.45 (5.0), n-hexane (10mL) | 0.80 (5.1), n-hexane (10mL) | n-hexane/benzene (5:1) | 2.20g (68.2) |
| $C_6H_5$ | 1.60 (2.3), benzene (10mL) | 0.38 (2.4), n-hexane (10mL) | benzene | 0.75g (37.9) |

Crystal Data Collection and Structure Determination of Bis-[O,O'-diphenyldithiophosphato]tin(II), $Sn[S_2P(OC_6H_5)_2]_2$

Colorless, prismatic crystals were obtained by crystallization from a hexane/toluene (1:1) mixture at 0°C. Crystal data are given in Table VI. Data were collected at 138 ± 2K with a CAD-4 counter diffractometer (Enraf-Nonius) controlled by a PDP8/e computer and fitted with a low-temperature apparatus. Details of the method of data collection and data reduction have been reported previously.[11] Pertinent data collection parameters are given in Table VII.

The structure was determined by conventional Patterson and Fourier techniques. Refinement was concluded at an R factor of 0.029 over all data, when shifts in the positional and thermal parameters of the non-hydrogen atoms were less than one-third the corresponding estimated standard deviation. A final difference Fourier map contained no peaks of greater than 0.9 $e\text{Å}^3$. Scattering factors were for neutral atoms and were taken from refs. 12(Sn,C,P,O,S) and 13(H). The positional parameters for the non-hydrogen atoms are listed in Table VIII, the positional and isotropic thermal parameters for hydrogen in Table IX and the anisotropic thermal parameters for the non-hydrogen atoms in Table X. Internuclear distances are listed in Table XI and angles in Table XII.

## Results and Discussion

### Syntheses and Properties

The tin(II) dithiophosphate esters, $Sn[S_2P(OR)_2]_2$, are prepared in high yield by the action of dimethoxytin(II) on the O,O'-diorganodithiophosphoric acids in a 1:2 molar ratio in benzene (a suspected carcinogen) to release methanol:

$$(CH_3O)_2Sn + 2HS\overset{S}{\overset{\|}{P}}(OR)_2 \rightarrow Sn[S\overset{S}{\overset{\|}{P}}(OR)_2]_2 + 2CH_3OH$$

$$R = CH_3, C_2H_5, i\text{-}C_3H_7, C_6H_5 \qquad (1)$$

The $R = C_2H_5$ product is a pale yellow oil, but the others are colorless crystalline solids soluble in non-polar organic solvents. Analytical and physical data are listed in Table I.

2,2'-Bipyridyl adducts of the tin(II) derivatives form immediately on mixing solutions of the tin compounds and the ligand.

The proton NMR spectra consist as expected of the pattern of the organic ester groups in the appropriate integrated areas and peak multiplicities. For example, in the spectrum of bis-[O,O'-dimethyldithiophosphato]tin(II), $Sn[S\overset{S}{\overset{\|}{P}}(OCH_3)_2]_2$, the methoxy group signal appears as a doublet at 3.50ppm arising from coupling to phosphorus $|^3J(^{31}P\text{-}O\text{-}C\text{-}^1H)|$=15.5Hz, a value apparently unaffected by the oxidation state of the attached tin atom since the tri-[14] and diphenyltin(IV)[15] analcgues displays the same coupling constant. In the ethoxy derivative, however, the methylene protons appear as a doublet of quartets arising from a coupling to phosphorus-31 of 10.0Hz and a coupling with the terminal/methyl protons, $|^3J(^1H\text{-}C\text{-}C\text{-}^1H)|$= 7.0Hz, again identical values to those found in the tri-[14] and diphenyltin(IV)[15] analogues.

In the infrared spectra it is unfortunately impossible to assign the positions of the ν(P-S) and ν(P=S) modes with confidence, and hence a discussion of the possible structural possibilities cannot be mounted on this basis. The infrared absorptions are listed in Table IV and some selected assignments for the four dithiophosphate esters are presented in Table XIII. The P-S absorptions which appear in the 670-630 and 560-530 $cm^{-1}$ ranges whether for the free acids, $HS\overset{S}{\overset{\|}{P}}(OR)_2$, their esters, $RS\overset{S}{\overset{\|}{P}}(OR)_2$[16-18] or for their transition metal complexes, $M[S_2P(OR)_2]_n$, in which the bidentate ligands chelate,[19] can be found at 660-627 and 525-505 $cm^{-1}$ in the tin(II) derivatives, and are described as $\nu_{asym}(PS_2)$ and $\nu_{sym}(PS_2)$, respectively. The ν[(P)-O-C] and ν[P-O(C)] modes have been assigned to the 1190-1152 and 1025-1010 $cm^{-1}$ ranges in our compounds, respectively, with reference to the data in ref. 20. However, other authors claim that these modes absorb in the 1060-905 and 875-730 $cm^{-1}$ regions, respectively, while bands occurring in the range 1240-1085 $cm^{-1}$ arise from deformation vibrations

involving the carbon atom of the P-O-C linkage.[21] The assignment of our $\nu(PS_2)$ modes is done by analogy with those reported for the corresponding organolead,[22] -thallium[18] and -mercury[23] derivatives.

Mass spectral data for the four tin(II) compounds are listed in Table V with suggested assignments. Even electron parent molecular ions are found in all the spectra, unlike our experience with the analogous di-[15] and triorganotin(IV)[14] species. Moreover, loss of a neutral alkane to form a further even electron ion in both cases where this is possible (R = $C_2H_5$, $\underline{i}$-$C_3H_7$) is unusual in spectra normally dominated by even electron species. The fragments resulting from the loss of one ligand moiety are the most abundant tin-bearing ions in all the spectra but that of the isopropoxy derivative, as with the di-[15] and triorganotin(IV)[14] species. Common fragments include the $SnS_2PO^+$ (m/e=231) and $Sn^+$ (120) ions. The chief pathway for the decomposition of these esters is the successive loss of ligand moieties.

Most interesting from a structural point of view are two even electron ions of low relative abundance at m/e=581 and 553 in the mass spectrum of the diethoxy ester. These fragments exhibit the characteristic patterns of a ditin-bearing ion, and are assigned as $\{Sn_2L[S_2P(O)OC_2H_5]\}^+$ and $\{Sn_2L[S_2P(O)OH]\}^+$. This observation suggests an associated structure for the tin(II) esters (vide infra).

The mass spectra of the bipyridyl adducts are the superposition of the fragmentation patterns of the parent tin(II) dithiophosphate derivatives and of bipyridyl with only small differences in relative abundances. These data have thus not been separately tabulated.

The tin-119m Mössbauer data gathered in Table II confirm that the tin(II) oxidation state is present.[24] The Isomer Shifts (IS) lie in the range 3.66-3.78 mm $s^{-1}$, and the Quadrupole Splittings (QS) are just resolvable (0.97-1.06mm $s^{-1}$) and do not increase on complexation by bipyridyl. This suggests that the coordination number at the tin atom does not change on going from the dithiophosphate esters to their bipyridyl adducts, and thus that the parent tin(II) esters are of higher coordination number in the solid state (vide infra). The

coordination number at the tin atom in the bipyridyl adducts must be at least $\psi$-5 [with two monodentate dithiophosphate ester ligands, a bidentate nitrogenous ligand and the lone pair about tin(II)], although higher coordinations are both possible and more likely utilizing one or both dithiophosphate moieties in the usual bidentate mode.[19] Thus the coordination about the tin(II) atom in the parent esters must also be at least $\psi$-5, involving two bidentate sulfur ligands (vide infra).

The Crystal and Molecular Structure of Bis-[O,O'-diphenyldithiophosphate]tin(II), $Sn[S_2P(OC_6H_5)_2]_2^2$

The title compound exists as a centrosymmetric dimer as depicted in Figure 1 and shown packed into the unit cell in Figure 2. Each of the tin(II) atoms in the dimer is bound to two dithiophosphate ligands: one binding tin in a simple, chelating, anisobidentate fashion, while a second ligand is extremely skewed, with one of the sulfur atoms S(4) bridging to the tin(II) atom of an adjacent molecule to form a rectangular $Sn_2S_2$ ring, and at the same time chelating the tin(II) atom to which the ligand is ester bound (see Figure 1). Completing the coordination sphere of the tin(II) atom, and contributing to the formation of the dimer is a $\underline{h}^6$-$C_6H_5$ interaction between the phenoxy ester group of the bridging ligand of the second molecule and the tin(II) lone pair as depicted in Figure 1. This produces a distorted $\psi$-6 geometry at the metal center. The planar $Sn_2S_2$ ring which contains triply bonded sulfur atoms can be seen in Figure 1 to be circumscribed by an eight-membered $[SnSPS]_2$ ring in a chair conformation.

We first discuss the simple, terminally-chelated system whose understanding requires the identification of the sulfur atoms in terms of their belonging to the covalently bound ester system, $>\overset{S}{\underset{|}{P}}-S-Sn$, or to the datively bound, $>\overset{S}{\underset{|}{P}} = S \rightarrow Sn$, system. It is known for the dithiophosphate ester derivatives of the transition metals that the more tightly the sulfur atom is bound to the metal atom, then the longer is its bond with phosphorus.[19] Conversely, the shorter sulfur bonds to

phosphorus can be written as P=S, and are associated with the longer, coordinate covalent sulfur-metal interaction. These shorter, P=S distances are found in the range 1.85-1.95 Å for the dithiophosphate ester complexes, with the corresponding single, P-S distances at 1.99-2.19 Å.[19] More direct comparison is made in Table XIV with the internuclear distances in the ester P-S-Sn and dative P=S→Sn linkages from four recent molecular structure determinations of dithiophosphate ester derivatives of tin(IV)[25-27] from this laboratory, plus another from the literature.[28] Except for bis-[O,O'-diisopropyldithiophosphato]diphenyltin(IV), $[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_5)_2$, in which the ligands chelate symmetrically,[26] the ester and dative portions of these chelating ligands can be easily distinguished.

The bonds that sulfur makes with tin(II) are expected to be longer than for their tin(IV) analogues, since their covalent radii have been assigned as 1.63 and 1.40 Å, respectively.[29] Examination of Table XIV, however, reveals no such apparent difference, since for both the ester and dative tin-sulfur bonds, longer tin(IV) examples are available in genuinely chelating systems. The title compound fits our model in that the long, dative S(2)-Sn(1) [2.8300(6) Å] bond is associated with the shorter P(1) = S(2) [1.9670(8) Å] bond, and the short S(1)-Sn(1) [2.6230(6) Å] ester bond is contiguous to a longer P(1)-S(1) [2.0016(8) Å] bond.

Turning to the bridging/chelating dithiophosphate ligand, with the same analysis, examination of Table XIV reveals consistent behavior here, too, in that the longer, dative, chelating S(4)-Sn(1) [3.3914(6) Å] bond is contiguous to the short P(2) = S(4) [1.9636(8) Å], and the shorter, S(3)-Sn(1) [2.6510(6) Å ester bond is associated with the long P(2)-S(3) [2.0064(8) Å] bond. The bridging S(4)-Sn(1') [3.0428(7) Å] bond is significantly longer than the corresponding bond S(2)-Sn(1) [2.8300 Å] in the terminally chelating system, but the P=S distances are quite similar. The unexpectedly long P(2) = S(4) [1.9636(8) Å] bond must arise because of electron withdrawal along the S(4)-Sn(1) vector at 3.3914 Å, thus confirming the chelating interaction between

these two atoms and the existence of the inner $Sn_2S_2$ ring. Thus the sulfur atom S(4) is involved simultaneously in binding both the tin(II) atoms in the dimer in a bifurcated, three-coordinated manner. The three-coordinated sulfur atoms that bridge two metal centers in $\{CuS_2P[OCH(CH_3)_2]_2\}_4$, on the other hand, form equal or stronger sulfur-metal bonds than the sulfurs bonded to only a single metal atom. In this case electron withdrawal from the bridging P=S bond so lengthens this distance that it actually becomes longer than the adjacent P-S single bond.[30]

Precedent for the bifurcated association and our three-coordinated sulfur atom can be found in the structure of the dimeric bis[tetrathiotungstato]tin(II) which contains tridentate $WS_4$ ligands.[31] Planar, four-membered $Sn_2S_2$ rings are found in $Sn_2S_3$,[32] $(t\text{-}C_4H_9)_2SSn$[33] and $(CH_3Sn)_4S_6$,[34] and the dimeric $[Cl_3SnPO_2Cl_2 \cdot POCl_3]_2$ contains an eight-membered centrosymmetric ring formed by the tin(IV) atoms and dichlorophosphate groups[35] like our $[SnSPS]_2$ system. Simple sulfur chelation of tin(II) atoms is found in the dithiocarbonate,[36] $Sn[S_2COCH_3]_2$, and carbamate,[37] $Sn[S_2CN(C_2H_5)_2]_2$. The structure of the title compound contrasts with those adopted by lead(II) diethyldithiophosphate in which the metal atoms are chelated in monomers,[38] and its diisopropyl analogue in which the metal atom is coordinated by six sulfur atoms, two of which are bonded intermolecularly to create a polymeric lattice.[39]

The sulfur atom coordination sphere about the tin(II) atom creates an $\psi$-6 situation with a distorted octahedral geometry and the lone pair of electrons occupying the sixth coordination site. The planar girdle of this octahedron can be considered to be formed by the four sulfur atoms S(1), S(2), S(4) and S(4'), with the tin atom 0.457 Å out of the least squares plane away from sulfur atom S(3). The sulfur atoms making ester bonds to the tin(II) atom in our analysis (vide supra) are cis-to one another [$\measuredangle$ S(1)-Sn(1)-S(3) = 87.41°].

The largest angle between adjacent (cis-) sulfur atoms is formed by S(2) and S(4') at 102.85°, while the smallest angle in the plane is formed by the terminally chelating system [ $\measuredangle$ S(1)-Sn(1)-S(2) = 74.28°]. The sulfur atom normal to this plane [S(3)] leans in the direction of S(4), making a rather acute angle [ $\measuredangle$ S(3)-Sn(1)-S(4) = 66.21°].

Sulfur atom S(3) is opposite the expected direction of the tin(II)-lone pair vector. This S(3)-Sn(1) vector when extended strikes near to the center of one of the phenyl groups of an ester of the bridging ligand of a second monomeric unit. This phenyl group is oriented in a spacially significant position nearly perpendicular to the assumed lone pair vector. A view of the tin coordination sphere looking roughly along the S(3)-Sn(1) bond is found in Figure 3, and approximately perpendicular to this vector in Figure 4. The phenyl group appears approximately centered over the lone pair, with tin to carbon distances ranging from 3.457 to 4.317 Å (mean 3.896 Å). The distance from the tin atom to the least squares center of the ring is 3.66 Å, and is perpendicularly 3.46 Å from the least squares plane of the ring. These distances are long when compared with those in $\underline{h}^6$-$C_6H_6$ transition metal complexes,[40] but are (in part) within the sum of the van der Waals radii (4.00 Å).[41,42]

Known π-Sn(II) to aromatic ring interactions are listed in Table XV. Expecially relevant are the structures of the polymeric materials of the composition $\underline{h}^6$-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$,[43] $C_6H_6SnCl(AlCl_4)$ and $\underline{h}^6$-$\underline{para}$-$(CH_3)_2C_6H_4SnCl(AlCl_4)$.[44] The first consists of pentagonal bipyramidal arrangements of six chlorine atoms about each tin with the last coordination site occupied by a symmetrically-placed benzene molecule. An additional benzene molecule of solvation fits into a cleft of the structure. The coordination number at the tin(II) atom is thus ψ-7.[43] In the latter two materials there are five chlorine atoms about each tin(II) with the sixth coordination site occupied by the aromatic moiety. The coordination number in this case is ψ-6, and the geometry is distorted octahedral.[44] In all three cases the tin(II)-carbon distances are very regular and the local symmetry

of the aromatic ring interaction is $C_{6v}$. A qualitative molecular orbital model which accommodates the tin(II) atom 5s, and 5p electrons, those from six chlorine atoms and those of the benzene ring in $\underline{h}^6$-$C_6H_5Sn(AlCl_4)_2 \cdot C_6H_6$ leads to a diamagnetic, closed-shell electronic structure with the principal interaction between the tin(II) atom and the benzene ring as an $e_1$ MO formed by overlap between p-orbitals lying in a plane parallel to the benzene ring and rationalizing the rather long tin-carbon distance.[43] This scheme contrasts with the generally accepted bonding model for transition metal aromatic complexes where metal d-orbitals are directed toward the carbon atoms. In the tin(II) case, only the $5p_x$ and $5p_y$-orbitals are available for interaction with the benzene $e_1$ electrons.

Our derivative is unusual, and different from the materials discussed above in two ways: Firstly, to our knowledge we have here the only example of an $\underline{h}^6$-$C_6H_5$ main group π-interaction; and secondly, the only known example of such an interaction contributing to the formation of a dimer from the constituent monomers.

The two phenyl rings which appear overlayed in the center of the cell in Figure 2 in fact occupy front and back regions and are separated by more than 12 Å.

The phosphorus atoms in the dithiophosphate ester ligands are found at the center of a distorted tetrahedral system with two oxygen atoms and two sulfur atoms, one of the latter double bonded. As we have found in other dithiophosphate ester derivatives of tin(IV),[25,26] the angles involving the more electronegative oxygen atoms are, as expected on the basis of isovalent hybridization, arguments, smaller than those involving the sulfur atoms. We find that in both the chelating and bridging ligands $\measuredangle$ S-P-S > $\measuredangle$ S-P-O (mean values) > $\measuredangle$ O-P-O.

Of the tin(II) dithiophosphate esters, only the phenoxy derivative is stable to air oxidation. The other analogues we have prepared turn an orange color on exposure to air, and the surface oxidation to produce an unidentified tin(IV) product, presumably of the $[(RO)_2PS_2]_2SnO$ variety, can be followed by Mössbauer

spectroscopy. The structure-reactivity relation which can rationalize the chemical stability of the phenoxy ester derivative must have to do either with additional lattice energy provided by the $\underline{h}^6$-$C_6H_5$ bonding interaction with the tin(II) atom or with the protection of the tin(II) lone pair of electrons by the steric bulk of the phenyl ring, or by both.

Our observation discussed above that the magnitude of the QS values remains unchanged in going from the tin(II) dithiophosphate esters to their bipyridyl adducts can now be understood in terms of the structure we have solved. If the coordination number at the tin(II) center is the same in the bipyridyl adduct as in the parent solids from which they are derived, then presuming that the bipyridal donor is itself bidentate, one of the dithiophosphate ester ligands must be monodentate in these adducts to produce the $\psi$-6 situation. Such a monodentate ligand is found in the structure of triphenyltin(IV) diethyldithiophosphate.[11] The more reasonable $\psi$-7 alternative, employing all ligands in a bidentate manner, is known for tin(II) in the structure of $\underline{h}^6$-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$.[43]

Supplemental Material. Listing of structure factor amplitudes ( pp.). Ordering information is given on any current masthead page.

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## References and Notes


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Table I. Analytical[a] and Physical Data for the Tin(II) Dithiophosphate Esters and Their Bipyridyl Adducts.

| Compound | Color | m.p. | %C[a] | %H[a] | %N[a] | Mol. Wt.[a] | Yield(%) |
|---|---|---|---|---|---|---|---|
| $Sn[S_2P(OCH_3)_2]_2$ | Colorless | 65.5-67° | 10.60(11.09) | 2.98(2.79) | | | 87 |
| $Sn[S_2P(OC_2H_5)_2]_2$ | Pale yellow | oil | 19.89(19.64) | 4.32(4.13) | | | 95 |
| $Sn[S_2P(O\text{-}i\text{-}C_3H_7)_2]_2$ | Colorless | 55-58° | 26.96(26.43) | 5.23(5.19) | | | 75 |
| $Sn[S_2P(OC_6H_5)_2]_2$ | Colorless | 125.5-126.5° | 42.50(42.31) | 3.10(2.96) | | 747(682)95 | |
| $Sn[S_2P(OCH_3)_2]_2 \cdot$2,2'-bipy | Yellow | 112-4° | 28.59(28.54) | 3.49(3.43) | 4.73(4.75) | | 51 |
| $Sn[S_2P(OC_2H_5)_2]_2 \cdot$2,2'-bipy | Orange | 113-4° | 34.23(33.50) | 4.53(4.38) | 5.10(4.34) | | 68 |
| $Sn[S_2P(O\text{-}i\text{-}C_3H_7)_2]_2 \cdot$2,2'-bipy | Yellow | 105-7° | 37.78(37.67) | 4.86(5.18) | 4.56(3.99) | | 73 |
| $Sn[S_2P(OC_6H_5)_2]_2 \cdot$2,2'-bipy | Yellow | 196-8°(dec) | 49.35(48.76) | 3.43(3.38) | 3.30(3.34) | | 40 |

[a]Calculated values in parentheses.

Table II. Tin-119m Mössbauer Data for the Tin(II) Dithiophosphate Esters and Their Adducts at 77K.

| Compound | IS | QS | $\Gamma_+$ | $\Gamma_-$ |
|---|---|---|---|---|
| $Sn[S_2P(OCH_3)_2]_2$ | 3.67 | 0.97 | | |
| $Sn[S_2P(OC_2H_5)_2]_2$ | | | | |
| $Sn[S_2P(O\text{-}\underline{i}\text{-}C_3H_7)_2]_2$ | 3.49 | 1.12 | 1.11 | 1.19 |
| $Sn[S_2P(OC_6H_5)_2]_2$ | 3.78 | 1.06 | | |
| $Sn[S_2P(OCH_3)_2]_2 \cdot$bipy | | | | |
| $Sn[S_2P(OC_2H_5)_2]_2 \cdot$bipy | 3.75 | 1.04 | 1.10 | 1.05 |
| $Sn[S_2P(OC_3H_7\text{-}i)_2]_2 \cdot$bipy | 3.66 | 1.03 | 0.97 | 1.05 |
| $Sn[S_2P(OC_6H_5)_2]_2 \cdot$bipy | 3.75 | 1.15 | 1.07 | 1.03 |

Table III. $^{1}H$ nmr Data for the Tin(II) Dithiophosphate Esters, $Sn[S_2P(OR)_2]_2$[a,b,c]

| R | |
|---|---|
| $CH_3$ | d, 3.50(12H,$POC\underline{H}_3$), $\lvert^3J(^{31}P\text{-}O\text{-}C\text{-}^{1}H)\rvert$ = 15.5. |
| $C_2H_5$ | dq, 4.13(8H,$POC\underline{H}_2CH_3$), $\lvert^3J(^{31}P\text{-}O\text{-}C\text{-}^{1}H)\rvert$ = 10.0, $\lvert^3J(^{1}H\text{-}C\text{-}C\text{-}^{1}H)\rvert$ = 7.0; t, 1.13(12H,$POCH_2C\underline{H}_3$), $\lvert^3J(^{1}H\text{-}C\text{-}C\text{-}^{1}H)\rvert$ = 7.0. |
| $i\text{-}C_3H_7$ | m, 5.00(4H,$POC\underline{H}(CH_3)_2$), $\lvert^3J(^{31}P\text{-}O\text{-}C\text{-}^{1}H)\rvert$ = 13.0, $\lvert^3J(^{1}H\text{-}C\text{-}C\text{-}^{1}H)\rvert$ = 6.5; d, 1.32(2H,$POCH(C\underline{H}_3)_2$), $\lvert^3J(^{1}H\text{-}C\text{-}C\text{-}^{1}H)\rvert$ = 6.5. |
| $C_6H_5$ | m, 6.84-7.55(20,$POC_6\underline{H}_5$) |

[a] In $C_6D_6$

[b] d = doublet, dq = doublet of quartets, m = multiplet

[c] $\delta$ in ppm; coupling constants in Hz

Table IV. Infrared Data[a] for the Tin(II) Dithiophosphate Esters, $Sn[S_2P(OR)_2]_2$ and Their Bipyridyl Adducts $Sn[S_2P(OR)_2]_2 \cdot C_{10}H_8N_2$

| | |
|---|---|
| $Sn[S_2P(OCH_3)_2]_2$[b]: | 1820w br, 1259 w, 1170 vs, 1045 sh, 1030 vvs br, 815 vs, 790 vvs br, 652 vs, 635 vs br, 505 s, 425 w, 360 m, 340 s, 285 sh, 258 m, 225 w $cm^{-1}$. |
| $Sn[S_2P(OC_2H_5)_2]_2$[c]: | 2990 s, 2940 m, 2905 m, 2875 w, 1810 vw br, 1475 m, 1455 sh, 1445 m, 1392 s, 1367 w, 1294 w, 1152 s, 1099 m, 1040 sh, 1020 vvs, 960 vvs, 812 s, 785 vs br, 645 vs, 525 m br, 442 w, 420 w, 396 vw, 375 w, 355 w, 265 w, 255 w, 248 w $cm^{-1}$. |
| $Sn[S_2P(O\text{-}i\text{-}C_3H_7)_2]_2$[b]: | 1740 w br, 1265 vw, 1180 s, 1140 s, 1100 s, 1015 vvs, 887 s, 782 s, 760 vs, 627 s br, 525 s br, 442 m br, 332 vw, 350 vvw $cm^{-1}$. |
| $Sn[S_2P(OC_6H_5)_2]_2$[b]: | 3055 w, 1935 w, 1890 vw, 1850 vw, 1780 vw, 1727 vw, 1577 vs, 1555 sh, 1540 sh, 1240 w, 1190 s, 1175 vvs, 1150 vvs, 1070 m, 1025 m, 1010 m, 980 w, 910 vvs, 892 vvs, 870 sh, 830 vw, 760 vs, 730 s, 688 s, 660 vs, 568 m, 525 m, 486 m, 430 vw, 355 w, 300 w br, 240 w $cm^{-1}$. |
| $Sn[S_2P(OCH_3)_2]_2 \cdot C_{10}H_8N_2$[d]: | 3110 m, 3080 sh, 3065 m, 3015 sh, 3010 m, 2985 m, 2945 s, 2900 m, 2840 m, 1980 w br, 1950 w br, 1595 s, 1575 sh, 1565 sh, 1490 mw, 1470 sh, 1463 sh, 1440 s, 1316 w, 1243 w, 1170 m, 1160 m, 1090 sh, 1040 sh, 1035 sh, 1020 sh, 1005 vs br, 756 vs br, 655 vs, 640 vs br, 543 m, 521 m $cm^{-1}$. |

Table IV (Con't)

| | |
|---|---|
| $Sn[S_2P(OC_2H_5)_2]_2 \cdot C_{10}H_8N_2$[d]: | 3110 sh, 3090 m, 3080 m, 3037 mw, 3030 mw, 2980 s, 2938 ms, 2900 ms, 1720 vw br, 1592 m, 1575 sh, 1560 sh, 1543 sh, 1490 sh, 1470 m, 1460 sh, 1433 s, 1381 m, 1310 w, 1280 vw, 1262 vw, 1245 vw, 1150 m, 1084 sh br, 1030 sh, 1010 vs br, 927 vs br, 810 sh, 758 vs br, 730 sh, 650 sh, 640 s br, 530 m br $cm^{-1}$. |
| $Sn[S_2P(O\text{-}\underline{i}\text{-}Pr)_2]_2 \cdot C_{10}H_8N_2$[d]: | 3100 m, 3070 m, 3058 s, 3030 sh, 3015 sh, 2975 vs, 2928 s, 2870 m, 2813 mw, 1735 w br, 1700 w br, 1595 s, 1560 m, 1490 mw, 1463 m, 1446 ms, 1368 s, 1316 m, 1260 vw, 1245 vw, 1212 vw, 1170 m, 1151 m, 1135 m, 1097 s, 1072 m, 1060 m, 1010 sh, 990 sh, 945 vvs br, 875 s, 745 s br, 730 sh, 648 sh, 620 s br, 530 m br $cm^{-1}$. |
| $Sn[S_2P(OC_6H_5)_2]_2 \cdot C_{10}H_8N_2$[d]: | 3110 sh, 3085 s, 3050 s, 3020 sh, 1940 w br, 1790 vw br, 1580 s br, 1560 sh, 1540 sh, 1469 s, 1452 sh, 1433 s, 1306 w br, 1235 sh, 1175 vs, 1152 vs br, 1100 sh, 1060 m, 1009 m br, 880 sh, 860 vs br, 825 sh, 705 s br, 717 s, 675 s, 650 s br, 620 sh, 585 sh, 550 m, 525 m $cm^{-1}$. |

[a] Relative intensities are indicated by s = strong, m = medium, w = weak, v = very, br = broad and sh = shoulder.

[b] Nujol mull on CsI plates.

[c] Neat liquid on CsI plates.

[d] KBr disc.

Table V. Mass Spectral Data for the Tin(II) Dithiophosphate Esters.[a]

| $Sn[S_2P(OCH_3)_2]_2$ | m/e | Assignment | Relative Abundance(%) |
|---|---|---|---|
| | 434 | $Sn[S_2P(OCH_3)_2]_2^+$ | 23.5 |
| | 309 | $Sn(S)S_2P(OCH_3)_2^+$ | 1.3 |
| | 277 | $SnS_2P(OCH_3)_2^+$ | 100 |
| | 247 | $SnS_2PO_2^+$ | 7.9 |
| | 231 | $SnS_2PO^+$ | 1.8 |
| | 215 | $SnS_2P^+$ | 0.9 |
| | 199 | $SnSPO^+$ | 1.8 |
| | 184 | $SnS_2^+$ | 4.7 |
| | 151 | $SnP^+$ | 13.5 |
| | 120 | $Sn^+$ | 4.2 |

| $Sn[S_2P(OC_2H_5)_2]_2$ | m/e | Assignment | Relative Abundance(%) |
|---|---|---|---|
| | 581 | $Sn_2L[S_2P(O)OC_2H_5]^+$? | 2.7 |
| | 553 | $Sn_2L[S_2P(O)OH]^+$? | 2.2 |
| | 490 | $Sn[S_2P(OC_2H_5)_2]_2^+$ | 27.3 |
| | 462 | $SnL[S_2P(OH)OC_2H_5]^+$ | 5.9 |
| | 340 | ? | 4.4 |
| | 305 | $SnS_2P(OC_2H_5)_2^+$ | 100 |
| | 277 | $SnS_2P(OH)OC_2H_5^+$ | 48.1 |
| | 249 | $SnS_2P(OH)_2^+$ | 32.3 |
| | 231 | $SnS_2PO^+$ | 13.0 |
| | 215 | $SnS_2P^+$ | 4.7 |
| | 199 | $SnSPO^+$ | 3.3 |
| | 184 | $SnS_2^+$ | 7.9 |
| | 153 | $SnSH^+$ | 13.2 |
| | 121 | $SnH^+$ | 5.0 |
| | 120 | $Sn^+$ | 4.0 |

Table V (Con't)

| $Sn[S_2P(OC_3H_7\text{-}\underline{i})_2]_2$ | m/e | Assignment | Relative Abundance(%) |
|---|---|---|---|
| | 546 | $Sn[S_2P(OC_3H_7)_2]_2^+$ | 16.0 |
| | 504 | $SnL[S_2P(OH)OC_3H_7]^+$ | 1.1 |
| | 333 | $SnS_2P(OC_3H_7)_2^+$ | 62.1 |
| | 291 | $SnS_2P(OH)OC_3H_7^+$ | 58.2 |
| | 281 | ? | 6.9 |
| | 263 | $281-H_2O$? | 3.3 |
| | 249 | $SnS_2P(OH)_2^+$ | 100 |
| | 231 | $SnS_2PO^+$ | 13.8 |
| | 215 | $SnS_2P^+$ | 3.8 |
| | 153 | $SnSH^+$ | 7.2 |
| | 121 | $SnH^+$ | 1.8 |
| | 120 | $Sn^+$ | 1.6 |

| $Sn[S_2P(OC_6H_5)_2]_2$ | m/3 | Assignment | Relative Abundance(%) |
|---|---|---|---|
| | 682 | $Sn[S_2P(OC_6H_5)_2]_2^+$ | 2.9 |
| | 401 | $SnS_2P(OC_6H_5)_2^+$ | 100 |
| | 307 | $(401-C_6H_6)^+$ | 7.7 |
| | 245 | $Sn(S)OC_6H_5^+$? | 4.1 |
| | 231 | $SnS_2PO^+$ | 3.7 |
| | 229 | $SnSC_6H_5^+$ | 3.9 |
| | 213 | $SnOC_6H_5^+$ | 23.2 |
| | 120 | $Sn^+$ | 0.7 |

[a] L = ligand moiety.

Table VI. Crystal Data.

| | |
|---|---|
| Formula | $C_{24}H_{20}O_4P_2S_4Sn$ |
| fw | 681.34 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| a, Å | 10.499(5)[a] |
| b, Å | 13.948(7)[a] |
| c, Å | 9.291(4)[a] |
| α, deg | 99.18(6)[a] |
| β, deg | 95.71(5)[a] |
| γ, deg | 91.80(5)[a] |
| V, $Å^3$ | 1334.8 |
| Z | 2 |
| $D_{calculated}$, g $cm^{-1}$ | 1.70 |
| μ, $cm^{-1}$ | 12.9 |

[a]Based upon ±2θ values of 48 reflections, and using $MoK\alpha_1$ radiation (λ = 0.70926 Å) at 138(2)K.

Table VII. Data Collection Parameters.

| | |
|---|---|
| Diffractometer | Enraf-Nonius CAD/4 |
| Radiation | $MoK_{\bar{\alpha}}$ (0.71069 Å) |
| Temperature, K | $138 \pm 2$ |
| Scan Technique | $\theta$-$2\theta$ |
| Limit | $0 \leq 2\theta \leq 53^{\circ}$ |
| Maximum Scan Time | 60 s |
| Scan Angle | $(0.80 + 0.20 \tan\theta)^{\circ}$ |
| Aperture Width | $(2.50 + 0.86 \tan\theta)$mm |
| Aperture Height | 4 mm |
| Aperture Distance | 173 mm |
| Monitor Reflection | 2 2 4 |
| Intensity Monitor Frequency | 50 s |
| Maximum Fluctuation in Monitor | 4.5% |
| Orientation Monitors | 200 reflections[a] |
| Number of Unique Data | 5517 |
| Number of Observed Data[b] | 5154 |
| Corrections | Lorentz |
| | Polarization |
| | Absorption (Sn,S,P) |
| | Anomalous Dispersion |

[a] New orientation matrix if angular change greater than $0.1^{\circ}$. Orientation matrix based upon 17 reflections.

[b] $I > 2\,\sigma(I)$; intensities assigned to unobserved data: $1.4\sigma(I)$.

Table VIII. Final Positional Parameters ($x10^4$) for Non-hydrogen Atoms in Bis-[O,O'-diphenyl-dithiophosphato]tin(II), $Sn[S_2P(OC_6H_5)_2]_2$.[a]

| Atom | x | y | z |
|---|---|---|---|
| Sn(1) | 4511.7(1) | 841.7(1) | 1899.7(2) |
| P(1) | 4049.5(6) | 2979.3(4) | 3662.2(6) |
| P(2) | 7426.8(5) | 1210.7(4) | 623.2(6) |
| S(1) | 2846.7(5) | 2208.0(4) | 2056.1(6) |
| S(2) | 5370.4(6) | 2180.7(4) | 4459.9(6) |
| S(3) | 5771.3(5) | 1858.2(4) | 267.0(6) |
| S(4) | 7260.7(6) | -153.4(4) | 895.3(7) |
| O(1) | 3270(2) | 3566(1) | 4879(2) |
| O(2) | 4746(2) | 3877(1) | 3147(2) |
| O(3) | 8298(2) | 1394(1) | -632(2) |
| O(4) | 8293(2) | 1778(1) | 2026(2) |
| C(1) | 2507(2) | 3116(2) | 5767(3) |
| C(2) | 1219(3) | 2957(2) | 5335(3) |
| C(3) | 451(3) | 2580(2) | 6272(3) |
| C(4) | 1001(4) | 2379(2) | 7604(3) |
| C(5) | 2292(4) | 2546(2) | 8010(3) |
| C(6) | 3074(3) | 2916(2) | 7088(3) |
| C(7) | 4027(2) | 4550(2) | 2443(3) |
| C(8) | 3566(3) | 5338(2) | 3284(3) |
| C(9) | 2906(3) | 6006(2) | 2564(4) |
| C(10) | 2734(3) | 5873(2) | 1051(4) |
| C(11) | 3216(3) | 5073(2) | 228(3) |
| C(12) | 3874(3) | 4404(2) | 924(3) |
| C(13) | 8215(2) | 790(2) | -2015(3) |

Table VIII (Con't)

| Atom | x | y | z |
|---|---|---|---|
| C(14) | 7289(3) | 927(2) | -3113(3) |
| C(15) | 7289(3) | 347(2) | -4477(3) |
| C(16) | 8192(3) | -343(2) | -4725(3) |
| C(17) | 9117(3) | -458(2) | -3602(3) |
| C(18) | 9132(2) | 105(2) | -2236(3) |
| C(19) | 8714(2) | 2765(2) | 2167(3) |
| C(20) | 8112(2) | 3446(2) | 3080(3) |
| C(21) | 8586(3) | 4402(2) | 3315(3) |
| C(22) | 9628(3) | 4667(2) | 2639(3) |
| C(23) | 10211(3) | 3976(2) | 1727(3) |
| C(24) | 9755(2) | 3010(2) | 1488(3) |

[a]Estimated standard deviations in parentheses.

Table IX. Final Positional ($x10^3$) and Isotropic Thermal Parameters for Hydrogen Atoms[a] in $Sn[S_2P(OC_6H_5)_2]_2$[b].

| Atom | x | y | z | $B_{ISO}$ |
|---|---|---|---|---|
| H(2) | 86(3) | 310(2) | 440(3) | 1.6(6) |
| H(3) | -47(3) | 250(2) | 602(4) | 3.2(7) |
| H(4) | 54(4) | 218(3) | 815(4) | 4.9(9) |
| H(5) | 271(4) | 234(3) | 896(4) | 4.5(9) |
| H(6) | 404(3) | 307(2) | 728(4) | 3.0(7) |
| H(8) | 358(3) | 541(2) | 438(3) | 2.2(6) |
| H(9) | 256(3) | 653(3) | 321(4) | 3.7(8) |
| H(10) | 226(3) | 629(3) | 49(4) | 3.7(8) |
| H(11) | 304(4) | 501(3) | -68(4) | 4.6(9) |
| H(12) | 412(3) | 390(2) | 40(3) | 2.2(6) |
| H(14) | 659(3) | 134(2) | -288(3) | 2.2(6) |
| H(15) | 670(3) | 42(3) | -507(4) | 4.1(9) |
| H(16) | 813(3) | -72(2) | -562(4) | 2.8(7) |
| H(17) | 963(3) | -87(2) | -375(3) | 2.7(7) |
| H(18) | 968(3) | 9(2) | -155(3) | 2.0(6) |
| H(20) | 733(3) | 324(2) | 358(3) | 2.6(7) |
| H(21) | 815(4) | 491(3) | 394(5) | 5.3(10) |
| H(22) | 993(3) | 528(2) | 277(4) | 2.9(7) |
| H(23) | 1090(3) | 414(2) | 128(3) | 2.2(6) |
| H(24) | 1016(3) | 252(2) | 102(3) | 2.3(6) |

[a] Hydrogen atoms are numbered corresponding to the carbon atoms to which they are bonded.

[b] Estimated standard deviations in parentheses.

Table X. Final Anisotropic Thermal Parameters ($x10^4$) for Non-hydrogen Atoms in $Sn[S_2P(OC_6H_5)_2]_2$[a,b]

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Sn(1) | 175(1) | 146(1) | 174(1) | 28(1) | 28(1) | 23(1) |
| S(1) | 114(3) | 172(3) | 136(3) | 30(2) | 12(2) | 5(2) |
| S(2) | 189(3) | 167(3) | 158(3) | 46(2) | -34(2) | 22(2) |
| S(3) | 140(3) | 161(3) | 182(3) | 48(2) | 28(2) | 46(2) |
| S(4) | 174(3) | 129(3) | 213(3) | 24(2) | 0(2) | 31(2) |
| P(1) | 134(3) | 133(3) | 106(3) | 31(2) | 25(2) | 17(2) |
| P(2) | 121(3) | 125(3) | 123(3) | 20(2) | 19(2) | 2(2) |
| O(1) | 232(9) | 137(7) | 144(8) | 35(6) | 88(7) | 17(6) |
| O(2) | 140(8) | 168(7) | 169(8) | 18(6) | 17(6) | 47(6) |
| O(3) | 179(8) | 173(7) | 158(8) | -10(6) | 63(7) | -14(6) |
| O(4) | 177(8) | 158(7) | 144(8) | 16(6) | -8(6) | 1(6) |
| C(1) | 276(13) | 118(10) | 135(11) | 8(8) | 89(9) | -2(8) |
| C(2) | 271(13) | 190(11) | 192(12) | 41(9) | 84(10) | 0(9) |
| C(3) | 340(15) | 227(13) | 364(16) | -30(11) | 208(13) | -55(11) |
| C(4) | 675(22) | 221(13) | 246(14) | -123(13) | 302(14) | -32(10) |
| C(5) | 692(23) | 249(13) | 131(12) | -81(13) | 84(13) | 25(10) |
| C(6) | 392(16) | 233(13) | 155(12) | -11(11) | 18(11) | 22(10) |
| C(7) | 142(11) | 171(10) | 206(12) | -13(8) | 9(9) | 85(9) |
| C(8) | 222(13) | 192(11) | 239(13) | 17(9) | -4(10) | 28(10) |
| C(9) | 245(14) | 175(12) | 460(17) | 18(10) | -21(12) | 71(11) |
| C(10) | 259(14) | 271(13) | 472(18) | -30(11) | -96(13) | 223(13) |
| C(11) | 351(16) | 384(15) | 255(14) | -50(12) | -36(12) | 186(12) |
| C(12) | 280(14) | 257(13) | 188(12) | 0(10) | 58(10) | 60(10) |
| C(13) | 168(11) | 149(10) | 154(11) | -3(8) | 54(9) | 2(8) |
| C(14) | 275(13) | 241(12) | 200(12) | 120(10) | 41(10) | 48(10) |

Table X (Con't)

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| C(15) | 385(16) | 303(13) | 179(12) | 113(12) | -54(11) | 37(10) |
| C(16) | 391(15) | 226(12) | 159(12) | 45(11) | 69(11) | -5(9) |
| C(17) | 263(13) | 197(12) | 278(13) | 87(10) | 105(11) | 15(10) |
| C(18) | 166(12) | 227(12) | 200(12) | 38(9) | 10(9) | 32(9) |
| C(19) | 154(11) | 157(10) | 144(11) | 11(8) | -36(8) | 19(8) |
| C(20) | 174(12) | 223(12) | 265(13) | 21(9) | 42(10) | -11(10) |
| C(21) | 275(14) | 199(12) | 387(16) | 49(10) | 57(12) | -52(11) |
| C(22) | 291(14) | 167(12) | 396(16) | -30(10) | -8(12) | 30(11) |
| C(23) | 184(13) | 305(13) | 279(14) | -51(10) | 13(10) | 54(11) |
| C(24) | 142(11) | 228(12) | 188(12) | 21(9) | 0(9) | -7(9) |

[a] Estimated standard deviations in parentheses.

[b] Anisotropic temperature factors are in the form $\exp-2\pi^2[U_{11}h^2a^{x^2} + \cdots\cdot 2U_{23}klb^*c^*]$.

Table XI. Final Intramolecular Distances (Å) in $Sn[S_2P(OC_6H_5)_2]_2$[a]

| | | | |
|---|---|---|---|
| Sn(1)-S(1) | 2.6230(6) | C(7)-C(8) | 1.374(3) |
| Sn(1)-S(2) | 2.8300(6) | C(7)-C(12) | 1.386(4) |
| Sn(1)-S(3) | 2.6510(6) | C(8)-C(9) | 1.394(4) |
| Sn(1)-S(4) | 3.3914(6) | C(9)-C(10) | 1.380(5) |
| Sn(1)-S(4')[b] | 3.0428(7) | C(10)-C(11) | 1.388(4) |
| | | C(11)-C(12) | 1.382(4) |
| P(1)-S(1) | 2.0016(8) | | |
| P(1)-S(2) | 1.9670(8) | C(13)-C(14) | 1.378(4) |
| P(2)-S(3) | 2.0064(8) | C(13)-C(18) | 1.384(3) |
| P(2)-S(4) | 1.9636(8) | C(14)-C(15) | 1.391(4) |
| | | C(15)-C(16) | 1.382(4) |
| P(1)-O(1) | 1.596(2) | C(16)-C(17) | 1.385(4) |
| P(1)-O(2) | 1.592(2) | C(17)-C(18) | 1.380(4) |
| P(2)-O(3) | 1.598(2) | | |
| P(2)-O(4) | 1.594(2) | C(19)-C(20) | 1.382(3) |
| | | C(19)-C(24) | 1.376(3) |
| O(1)-C(1) | 1.408(3) | C(20)-C(21) | 1.385(4) |
| O(2)-C(7) | 1.422(3) | C(21)-C(22) | 1.383(4) |
| O(3)-C(13) | 1.413(3) | C(22)-C(23) | 1.379(4) |
| O(4)-C(19) | 1.414(3) | C(23)-C(24) | 1.391(4) |
| C(1)-C(2) | 1.372(4) | | |
| C(1)-C(6) | 1.383(4) | Sn(1)-C(13') | 3.622(2) |
| C(2)-C(3) | 1.395(4) | Sn(1)-C(14') | 3.457(3) |
| C(3)-C(4) | 1.386(4) | Sn(1)-C(15') | 3.745(3) |
| C(4)-C(5) | 1.373(5) | Sn(1)-C(16') | 4.168(3) |
| C(5)-C(6) | 1.389(4) | Sn(1)-C(17') | 4.317(3) |
| | | Sn(1)-C(18') | 4.065(2) |
| | | Sn(1)-Sn(1') | 4.1536(2) |

[a] Estimated standard deviations in parentheses.
[b] Primed atoms are related to the corresponding unprimed atoms by the center of symmetry at (0,0,0).

Table XII. Final Intramolecular Angles (deg.) in $Sn[S_2P(OC_6H_5)_2]_2$[a]

| | | | |
|---|---|---|---|
| S(1)-Sn(1)-S(2) | 74.28(2) | S(3)-P(2)-S(4) | 115.51(4) |
| S(1)-Sn(1)-S(3) | 87.41(2) | S(3)-P(2)-O(3) | 107.72(7) |
| S(1)-Sn(1)-S(4) | 153.53(2) | S(3)-P(2)-O(4) | 111.47(7) |
| S(1)-Sn(1)-S(4')[b] | 79.23(2) | S(4)-P(2)-O(3) | 114.29(7) |
| S(2)-Sn(1)-S(3) | 91.14(2) | S(4)-P(2)-O(4) | 106.94(7) |
| S(2)-Sn(1)-S(4) | 102.85(2) | O(3)-P(2)-O(4) | 99.83(9) |
| S(2)-Sn(1)-S(4')[b] | 153.40(2) | | |
| S(3)-Sn(1)-S(4) | 66.21(2) | P(1)-O(3)-C(13) | 123.1(1) |
| S(3)-Sn(1)-S(4')[b] | 85.34(2) | P(1)-O(4)-C(19) | 123.3(1) |
| S(4)-Sn(1)-S(4')[b] | 99.79(2) | | |
| | | O(1)-C(1)-C(2) | 118.7(2) |
| Sn(1)-S(1)-P(1) | 87.88(3) | O(1)-C(1)-C(6) | 118.3(2) |
| Sn(1)-S(2)-P(1) | 82.88(3) | C(2)-C(1)-C(6) | 122.9(2) |
| | | C(1)-C(2)-C(3) | 118.4(2) |
| S(1)-P(1)-S(2) | 112.32(4) | C(2)-C(3)-C(4) | 119.6(3) |
| S(1)-P(1)-O(1) | 110.50(7) | C(3)-C(4)-C(5) | 120.8(3) |
| S(1)-P(1)-O(2) | 112.45(7) | C(4)-C(5)-C(6) | 120.4(3) |
| S(2)-P(1)-O(1) | 113.75(7) | C(5)-C(6)-C(1) | 117.9(3) |
| S(2)-P(1)-O(2) | 108.33(7) | | |
| O(1)-P(1)-O(2) | 98.78(9) | O(2)-C(7)-C(8) | 119.2(2) |
| | | O(2)-C(7)-C(12) | 118.1(2) |
| P(1)-O(1)-C(1) | 123.6(1) | C(8)-C(7)-C(12) | 122.7(2) |
| P(1)-O(2)-C(7) | 120.8(1) | C(7)-C(8)-C(9) | 117.9(2) |
| | | C(8)-C(9)-C(10) | 120.4(3) |
| Sn(1)-S(3)-P(2) | 94.33(3) | C(9)-C(10)-C(11) | 120.5(3) |
| Sn(1)-S(4)-P(2) | 74.76(2) | C(10)-C(11)-C(12) | 119.9(3) |
| Sn(1)-S(4)-Sn(1') | 80.21(1) | C(11)-C(12)-C(7) | 118.6(2) |
| Sn(1')-S(4)-P(2) | 96.06(3) | | |

Table XII (Con't)

| | | | |
|---|---|---|---|
| O(3)-C(13)-C(14) | 120.2(2) | O(4)-C(19)-C(20) | 118.0(2) |
| O(3)-C(13)-C(18) | 117.6(2) | O(4)-C(19)-C(24) | 119.7(2) |
| C(14)-C(13)-C(18) | 122.2(2) | C(20)-C(19)-C(24) | 122.0(2) |
| C(13)-C(14)-C(15) | 118.0(2) | C(19)-C(20)-C(21) | 118.3(2) |
| C(14)-C(15)-C(16) | 121.0(3) | C(20)-C(21)-C(22) | 120.7(3) |
| C(15)-C(16)-C(17) | 119.7(3) | C(21)-C(22)-C(23) | 120.0(3) |
| C(16)-C(17)-C(18) | 120.4(2) | C(22)-C(23)-C(24) | 120.1(3) |
| C(17)-C(18)-C(13) | 118.8(2) | C(23)-C(24)-C(19) | 118.8(2) |

[a] Estimated standard deviations in parentheses.

[b] Primed atoms are related to the corresponding unprimed atoms by the center of symmetry at (0,0,0).

Table XIII. Selected Infrared Assignments for the Tin(II) Dithiophosphate Esters, $Sn[S_2P(OR)_2]_2$[a]

| R=$CH_3$[b] | $C_2H_5$[c] | i-$C_3H_7$[b] | $C_6H_5$[b] | |
|---|---|---|---|---|
| | | | 1190s | |
| 1170vs | 1152s | 1180s | 1175vvs | ν[(P)O-C] |
| | | | 1150vvs | |
| 1030vvs,br | 1020vvs | 1015vvs | 1025m | ν[P-O(C)] |
| | | | 1010m | |
| 635vs,br | 645vs | 627s,br | 660vs | $\nu_{asym}(PS_2)$ |
| 505s | 525m,br | 525s,br | 525m | $\nu_{sym}(PS_2)$ |
| 340s | 355w | 332vw | 355w | ν(SnS) |

[a] Relative intensities are indicated by s = strong, m = medium, w = weak, v = very, br = broad.

[b] Nujol mull on CsI plates.

[c] Neat liquid on CsI plates.

Table XIV. Comparative Tin-Sulfur and Phosphorus-Sulfur Internuclear Distances in Dithiophosphorus Derivatives, Å.

| Compound | Ester[a] P——S | Ester[a] S——Sn | Dative[a] P=S | Dative[a] S→Sn | Ref. |
|---|---|---|---|---|---|
| $[(C_6H_5O)_2PS_2]_2Sn$(II) | 2.0016 | 2.6230[b] | 1.9670 | 2.8300[b] | c |
| | 2.0064 | 2.6510[d] | 1.9636 | 3.0428[d] | |
| $(C_2H_5O)_2PS_2Sn(C_6H_5)_3$[e] | 2.054 | 2.4582 | 1.931 | 5.326 | 25 |
| $[(C_2H_5O)_2PS]_2Sn(C_6H_5)_2$[f] | 2.04 | 2.48 | 1.92 | 3.20 | 28 |
| | 2.03 | 2.49 | 1.94 | 3.23 | |
| $[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_6)_2$[f] | 2.006 | 2.678 | 1.998 | 2.689 | 26 |
| $[(CH_3)_2PS_2]_2Sn(CH_3)_2$[f] | 2.047 | 2.482 | 1.969 | 3.334 | 27 |
| $[(C_2H_5)_2PS_2]_2SnI_2$[g] | 2.043 | 2.537 | 2.026 | 2.621 | 27 |
| | 2.044 | 2.533 | 2.032 | 2.593 | |

[a]The first number listed in each case is the P-S distance and the second is the S-Sn distance.

[b]Data for the terminal ligands.

[c]This work.

[d]Data for the bridging ligands.

[e]This compound is a rare example of a monodentate dithiophosphate ligand system.

[f]Trans-diorganotin groups.

[g]Cis-diiodotin configuration.

Table XV. π-Sn(II)-Carbon Ring Interactions.

| Compound | d(Sn-COR), Å[a] | Range: d(Sn-C), Å | Ref. |
|---|---|---|---|
| $\underline{h}^6$-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$ | 2.74 | 3.06±0.02 | 43 |
| $\underline{h}^6$-$C_6H_6SnCl(AlCl_4)$ | 2.90 | 3.05-3.39 | 44 |
| $\underline{h}^6$-para-$/(CH_3)_2C_6H_4SnCl(AlCl_4)$ | 2.77 | 2.92-3.27 | 44 |
| $(\underline{h}^5$-$C_5H_5)_2Sn$[b] | - | 2.71±0.02 | 45 |
| $(\underline{h}^5$-$C_5H_5)SnCl$ | - | 2.45-2.75 | 46 |
| $Sn[S_2P(OC_6H_5)_2]_2$ | 3.66 | 3.46-4.32 | c |

[a] COR = Center of the six-membered ring.

[b] From electron diffraction data.

[c] This work.

## Figure Captions

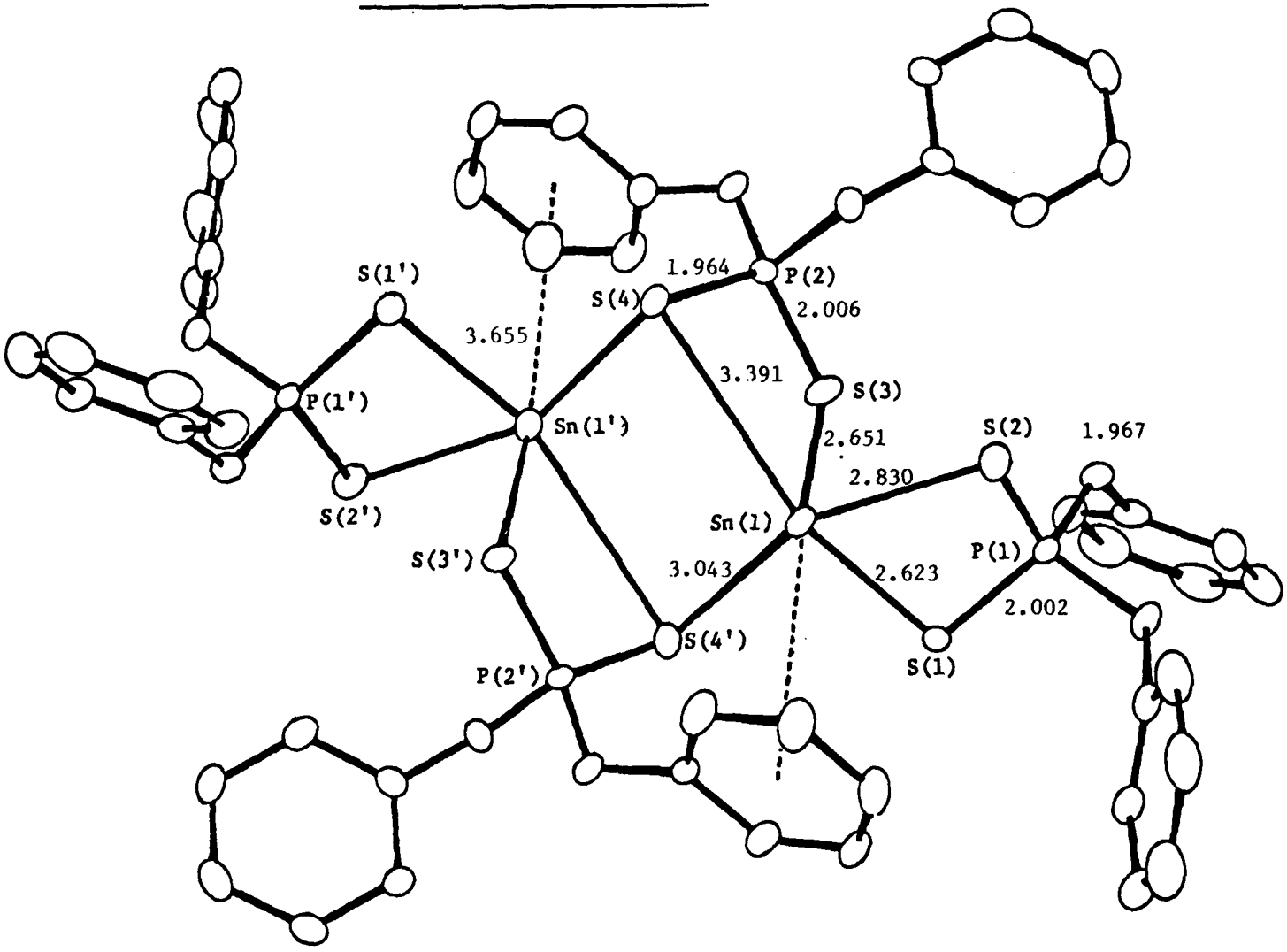
Figure 1. The molecular structure of dimeric bis-[O,O'-diphenyldithiophosphato] tin(II), $\{Sn[S_2P(OC_6H_5)_2]_2\}_2$, held together by bifurcated, three-coordinated sulfur atoms and $\underline{h}^6$-$C_6H_5$ interactions with the tin(II) lone pairs. Primed atoms are related to the corresponding unprimed atoms by the center of symmetry at (0,0,0).

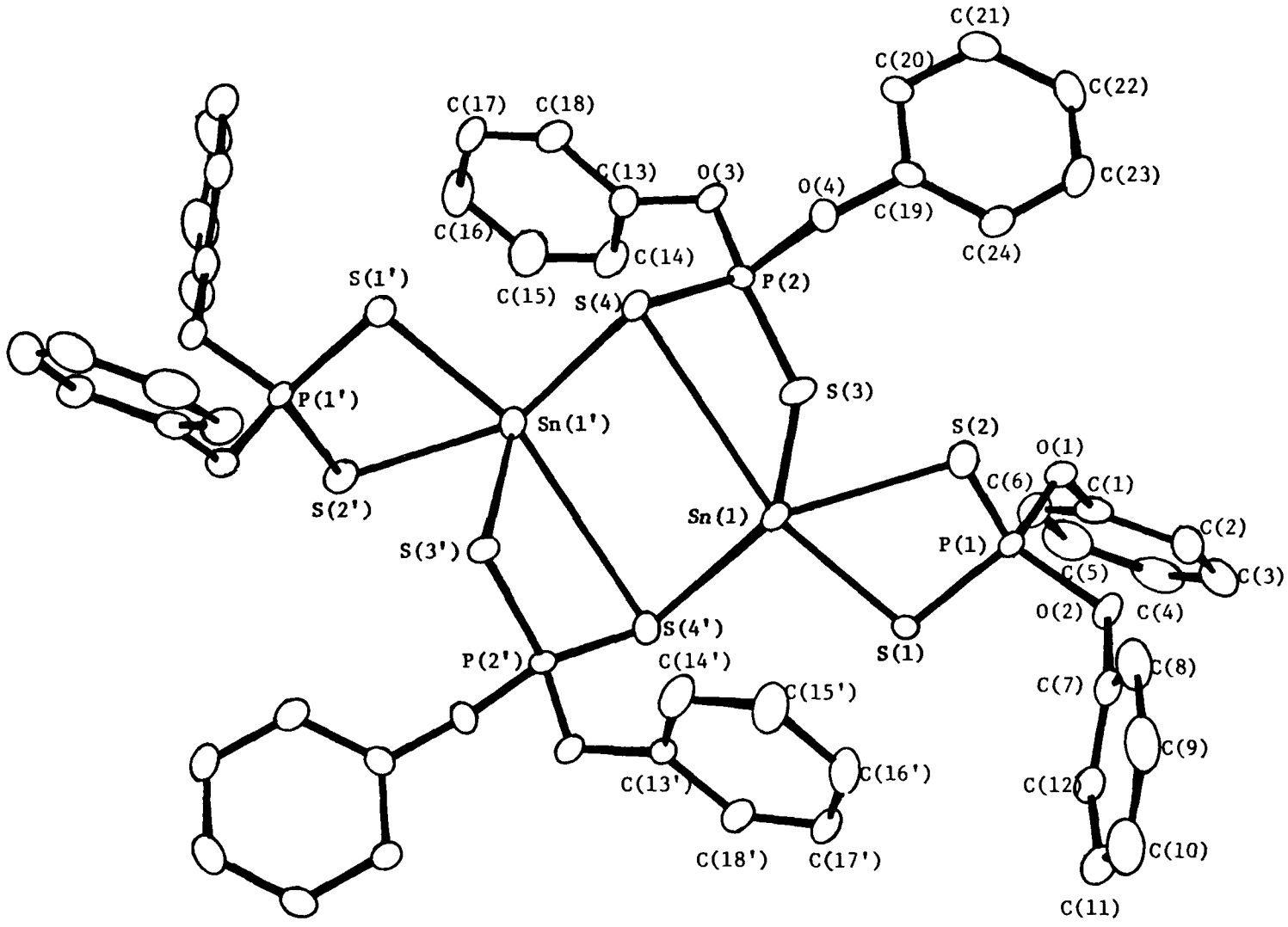
Figure 2. The contents of the unit cell showing the molecular packing.

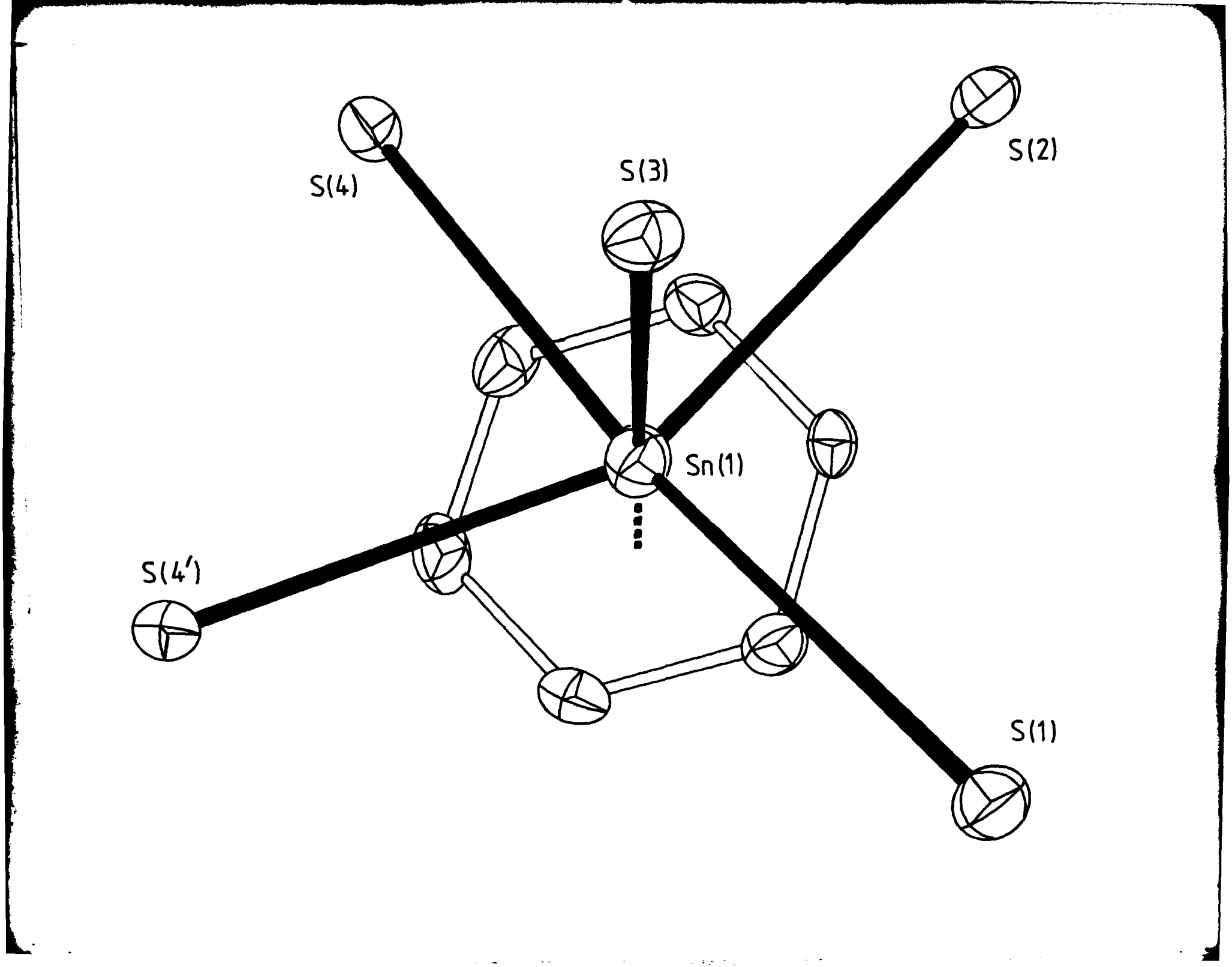
Figure 3. The $\underline{h}^6$-$C_6H_5$-tin(II) interaction along the S(3)-Sn(1) vector. The distance to the center of the ring is 3.655 Å.

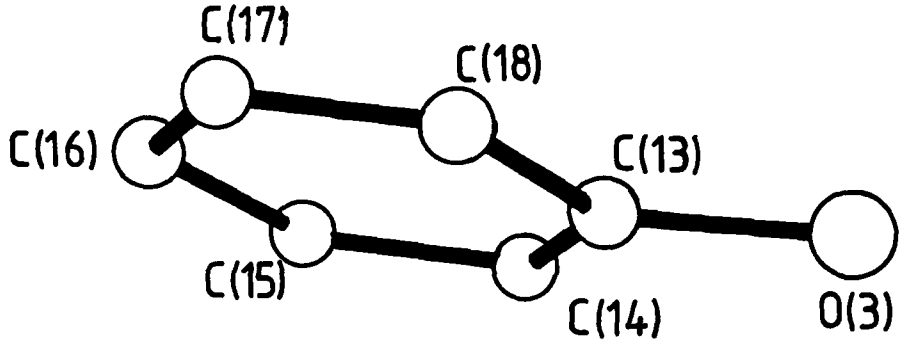
Figure 4. The $\underline{h}^6$-$C_6H_5$-tin(II) interaction viewed perpendicular to the S(3)-Sn(1) vector.

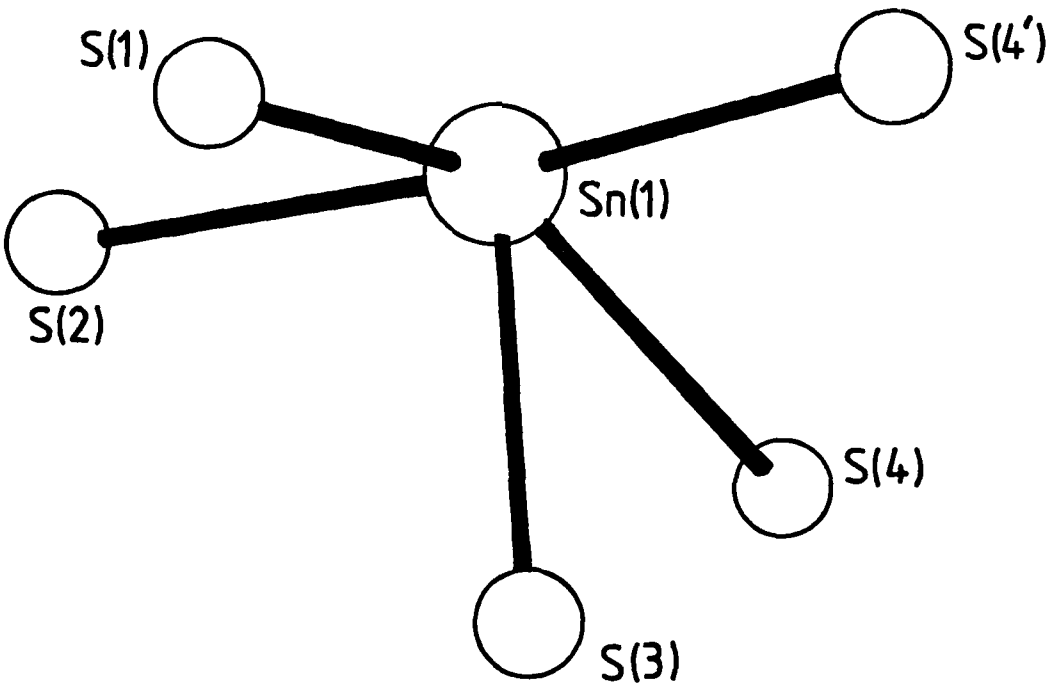
# $Sn[S_2P(OC_6H_5)_2]_2$

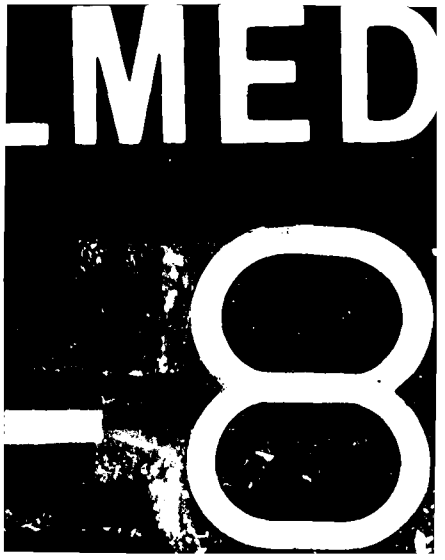



C(21)
C(20)
C(22)
C(17)
C(18)
C(23)
C(13)
O(3)
O(4)
C(19)
C(16)
C(14)
C(24)
C(15)
S(1')
S(4)
P(2)
P(1')
S(3)
Sn(1')
S(2)
O(1)
C(6)
C(1)
S(2')
Sn(1)
C(2)
P(1)
S(3')
C(5)
C(3)
O(2)
C(4)
S(4')
S(1)
P(2')
C(14')
C(8)
C(7)
C(15')
C(9)
C(16')
C(13')
C(12)
C(10)
C(18')
C(17')
C(11)


S(4)
S(3)
S(2)
Sn(1)
S(4')
S(1)


C(17)
C(18)
C(16)
C(13)
C(15)
C(14)
O(3)


S(1)
S(4')
Sn(1)
S(2)
S(4)
S(3)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